Monte Carlo in different ensembles

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Different Ensembles

Ensemble	Name	Constant (Imposed)	Fluctuating (Measured)
NVT	Canonical	N,V,T	P
NPT	Isobaric-isothermal	N,P,T	V
μVT	Grand-canonical	μ,V,T	N

Statistical Thermodynamics

Partition function

$$Q_{NVT} = \frac{1}{\Lambda^{3N} N!} \int \mathrm{dr}^N \exp\left[-\beta U\left(\mathrm{r}^N\right)\right].$$

I will come back to this

Ensemble average

$$\left\langle A \right\rangle_{NVT} = \frac{1}{Q_{NVT}} \frac{1}{\Lambda^{3N} N!} \int \mathrm{dr}^N A\left(\mathrm{r}^N\right) \exp\left[-\beta U\left(\mathrm{r}^N\right)\right].$$

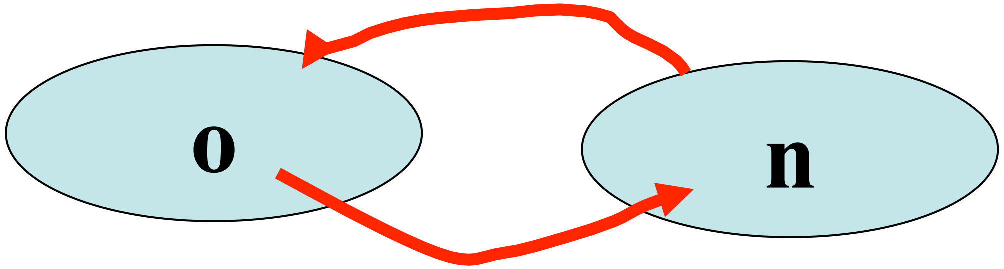
Probability to find a particular configuration

$$\mathrm{N}\left(\mathrm{r}^N\right) = \frac{1}{Q_{NVT}} \frac{1}{\Lambda^{3N} N!} \int \mathrm{dr'}^N \delta\left(\mathrm{r'}^N - \mathrm{r}^N\right) \exp\left[-\beta U\left(\mathrm{r'}^N\right)\right] \propto \exp\left[-\beta U\left(\mathrm{r}^N\right)\right]$$

Free energy

$$\beta F = -\ln\left(Q_{NVT}\right)$$

Detailed balance



$$K(o \rightarrow n) = K(n \rightarrow o)$$

$$K(o \rightarrow n) = N(o) \times \alpha(o \rightarrow n) \times \mathrm{acc}(o \rightarrow n)$$

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$$\frac{\mathrm{acc}(o \rightarrow n)}{\mathrm{acc}(n \rightarrow o)} = \frac{N(n) \times \alpha(n \rightarrow o)}{N(o) \times \alpha(o \rightarrow n)} = \frac{N(n)}{N(o)}$$

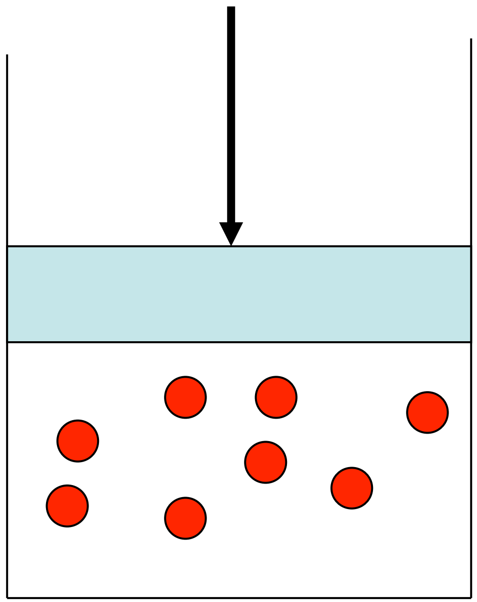
NVT-ensemble

$$N(n) \propto \exp\left[-\beta U\left(n\right)\right]$$

$$\frac{\mathrm{acc}(o \rightarrow n)}{\mathrm{acc}(n \rightarrow o)} = \frac{N(n)}{N(o)}$$

$$\frac{\mathrm{acc}(o \rightarrow n)}{\mathrm{acc}(n \rightarrow o)} = \exp\left[-\beta\left[U\left(n\right) - U\left(o\right)\right]\right]$$

NPT ensemble



We control the

- Temperature (T)
- Pressure (P)
- Number of particles (N)

Scaled coordinates

Partition function

$$Q_{NVT} = \frac{1}{\Lambda^{3N} N!} \int \mathrm{d}\mathrm{r}^N \exp\left[-\beta U\left(\mathrm{r}^N\right)\right].$$

Scaled coordinates

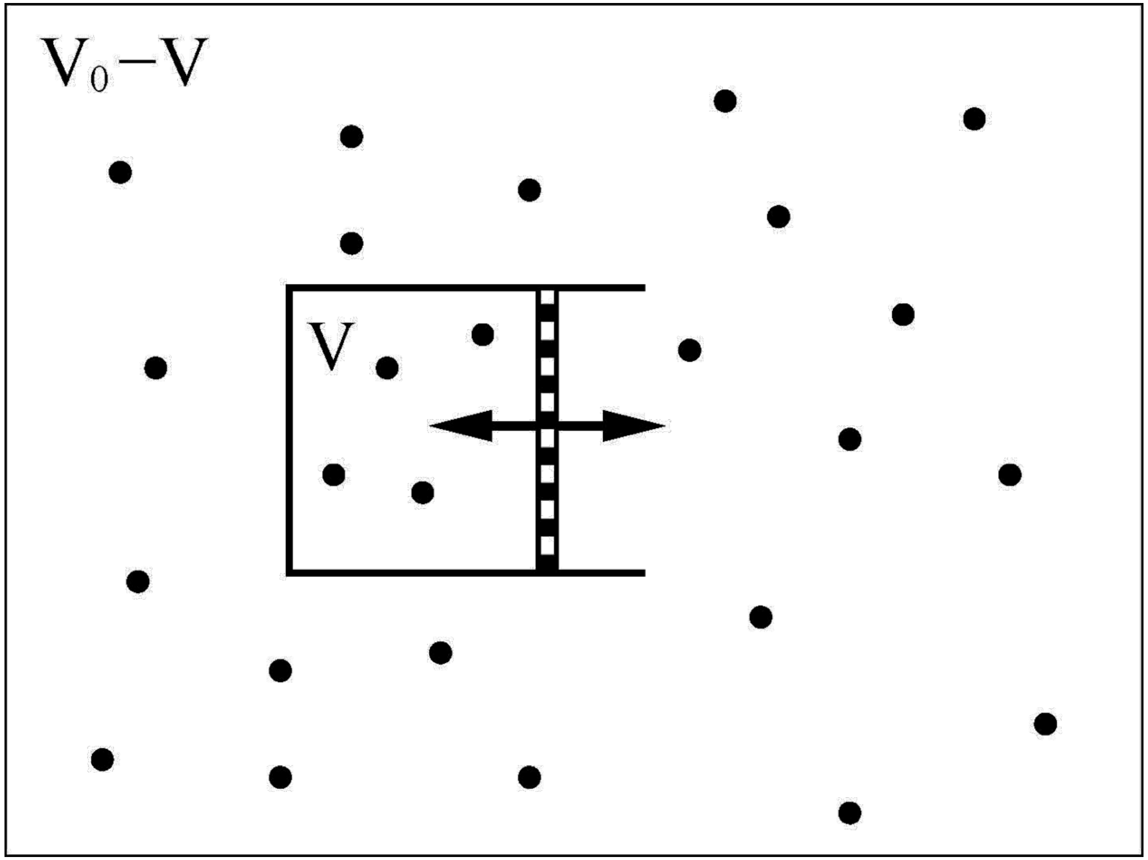
$$\mathbf{s}_i = \mathbf{r}_i / L$$

This gives for the partition function

$$Q_{NVT} = \frac{L^{3N}}{\Lambda^{3N} N!} \int \mathrm{d}\mathrm{s}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

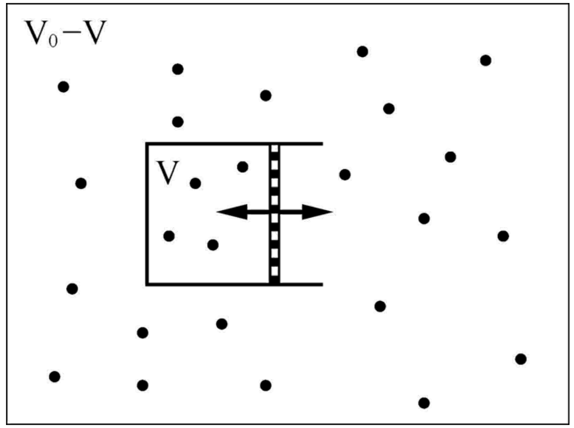
$$= \frac{V^N}{\Lambda^{3N} N!} \int \mathrm{d}\mathrm{s}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

The energy depends on the real coordinates



N in volume V

M in volume V_0-V



$$Q_{NVT}=\frac{V^N}{\Lambda^{3N}N!}\int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N;L\right)\right]$$

$$Q_{MV_0,NV,T}=\frac{\left(V_0-V\right)^{M-N}}{\Lambda^{3(M-N)}\left(M-N\right)!}\int \mathrm{ds}^{M-N}\exp\left[-\beta U_0\left(\mathrm{s}^{M-N};L\right)\right]\frac{V^N}{\Lambda^{3N}N!}$$

$$\times\int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N;L\right)\right]$$

$$Q_{MV_0,NV,T} = \frac{\left(V_0 - V\right)^{M-N}}{\Lambda^{3(M-N)}\left(M-N\right)!} \frac{V^N}{\Lambda^{3N} N!} \int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

To get the Partition Function of this system, we have to integrate over all possible volumes:

$$Q_{MV_0,N,T} = \int \mathrm{d}V \frac{\left(V_0 - V\right)^{M-N}}{\Lambda^{3(M-N)}\left(M-N\right)!} \frac{V^N}{\Lambda^{3N} N!} \int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

Now let us take the following limits:

$$\left.\begin{matrix} M \rightarrow \infty \\ V_0 \rightarrow \infty \end{matrix}\right\} \rho = \frac{M}{V} \rightarrow \text{constant}$$

As the particles in the reservoir are an ideal gas, we have:

$$\rho = \beta P$$

$$Q_{MV_0,N,T} = \int \mathrm{d}V \frac{\left(V_0 - V\right)^{M-N}}{\Lambda^{3(M-N)}\left(M-N\right)!} \frac{V^N}{\Lambda^{3N} N!} \int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

We have

$$\left(V_0 - V\right)^{M-N} = V_0^{M-N}\left(1 - V/V_0\right)^{M-N} \approx V_0^{M-N} \exp\left[-\left(M-N\right)V/V_0\right]$$

$$\left(V_0 - V\right)^{M-N} \approx V_0^{M-N} \exp\left[-\rho V\right] = V_0^{M-N} \exp\left[-\beta P V\right]$$

This gives:

$$Q_{NPT} = \frac{\beta P}{N!\Lambda^{3N}} \int \mathrm{d}V \exp\left[-\beta P V\right] V^N \int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

NPT Ensemble

Partition function:

$$Q_{NPT} = \frac{\beta P}{N!\Lambda^{3N}} \int \mathrm{d}V \exp\left[-\beta PV\right] V^N \int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

Probability to find a particular configuration:

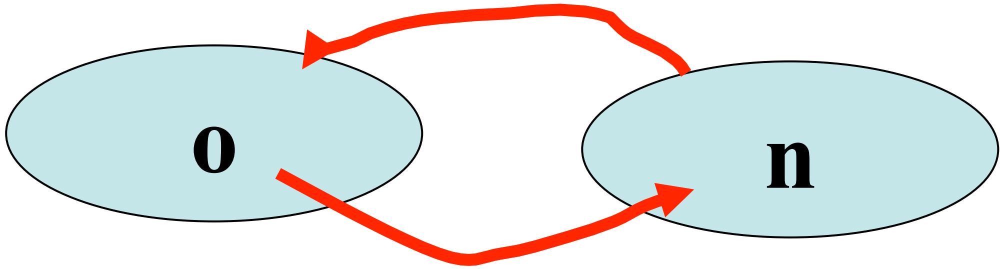
$$N_{NPT}\left(V, \mathbf{s}^N\right) \propto V^N \exp\left[-\beta PV\right] \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

Sample a particular configuration:

- change of volume
- change of reduced coordinates

Acceptance rules ??

Detailed balance



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$$\frac{\mathrm{acc}(o \rightarrow n)}{\mathrm{acc}(n \rightarrow o)} = \frac{N(n) \times \alpha(n \rightarrow o)}{N(o) \times \alpha(o \rightarrow n)} = \frac{N(n)}{N(o)}$$

NPT-ensemble

$$N_{NPT}\left(V,\mathbf{s}^N\right)\propto V^N\exp\left[-\beta PV\right]\exp\left[-\beta U\left(\mathrm{s}^N;L\right)\right]$$

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)}=\frac{N(n)}{N(o)}$$

Suppose we change the position of a randomly selected particle

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)}=\frac{\cancel{V^N\exp\left[-\beta PV\right]}\exp\left[-\beta U\left(\mathrm{s}_\mathrm{n}^\mathrm{N};L\right)\right]}{\cancel{V^N\exp\left[-\beta PV\right]}\exp\left[-\beta U\left(\mathrm{s}_\mathrm{o}^\mathrm{N};L\right)\right]}$$

$$=\frac{\exp\left[-\beta U\left(\mathrm{s}_\mathrm{n}^\mathrm{N};L\right)\right]}{\exp\left[-\beta U\left(\mathrm{s}_\mathrm{o}^\mathrm{N};L\right)\right]}=\exp\left\{-\beta\left[U(n)-U(o)\right]\right\}$$

NPT-ensemble

$$N_{NPT}\left(V,\mathbf{s}^N\right)\propto V^N \exp\left[-\beta PV\right]\exp\left[-\beta U\left(\mathrm{s}^N;L\right)\right]$$

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)}=\frac{N(n)}{N(o)}$$

Suppose we change the ***volume*** of the system

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)}=\frac{V_n{}^N \exp\left[-\beta PV_n\right]\exp\left[-\beta U\left(\mathrm{s}^{\mathrm{N}};L_n\right)\right]}{V_o{}^N \exp\left[-\beta PV_o\right]\exp\left[-\beta U\left(\mathrm{s}^{\mathrm{N}};L_o\right)\right]}$$

$$=\left(\frac{V_n}{V_o}\right)^N \exp\left[-\beta P\left(V_n-V_o\right)\right]\exp\left\{-\beta\left[U\left(n\right)-U\left(0\right)\right]\right\}$$

Algorithm: NPT

- Randomly change the position of a particle
- Randomly change the volume

Algorithm 10 (Basic NPT-Ensemble Simulation)

```
  PROGRAM mc_npt                   basic NPT ensemble simulation

  do icycl=1,ncycl                 perform ncycl MC cycles
    ran=ranf()*(npart+1)+1
    if (ran.le.npart) then
      call mcmove                  perform particle displacement
    else
      call mcvol                   perform volume change
    endif
    if (mod(icycl,nsamp).eq.0)
+     call sample                  sample averages
  enddo
  end
```

Algorithm 2 (Attempt to Displace a Particle)

```
 SUBROUTINE mcmove                 attempts to displace a particle

 o=int(ranf()*npart)+1             select a particle at random
 call ener(x(o),eno)               energy old configuration
 xn=x(o)+(ranf()-0.5)*delx         give particle random displacement
 call ener(xn,enn)                 energy new configuration
 if (ranf().lt.exp(-beta          acceptance rule (3.2.1)
+    *(enn-eno)) x(o)=xn           accepted: replace x(o) by xn
 return
 end
```

Comments to this algorithm:

1. *Subroutine* `ener` *calculates the energy of a particle at the given position.*
2. *Note that, if a configuration is rejected, the old configuration is retained.*
3. *The* `ranf()` *is a random number uniform in* $[0, 1]$.

Algorithm 11 (Attempt to Change the Volume)

```
SUBROUTINE mcvol                          attempts to change
                                          the volume
call toterg(box,eno)                      total energy old conf.
vo=box**3                                 determine old volume
lnvn=log(vo)+(ranf()-0.5)*vmax            perform random walk in ln V
vn=exp(lnvn)
boxn=vn**(1/3)                            new box length
do i=1,npart
  x(i)=x(i)*boxn/box                      rescale center of mass
enddo
call toterg(boxn,enn)                     total energy new conf.
arg=-beta*((enn-eno)+p*(vn-vo)
+ -(npart+1)*log(vn/vo)/beta)             appropriate weight function!
if (ranf().gt.exp(arg)) then              acceptance rule (5.2.3)
  do i=1,npart                            REJECTED
    x(i)=x(i)*box/boxn                    restore the old positions
  enddo
endif
return
end
```

Measured and Imposed Pressure

- Imposed pressure P
- Measured pressure <P> from virial

$$\left\langle P \right\rangle = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = \frac{-\int dV V^N e^{-\beta PV} \left(\int ds^N e^{-\beta U(s^N)}\right)\left(\frac{\partial F}{\partial V}\right)_{N,T}}{\int dV V^N e^{-\beta PV} \int ds^N e^{-\beta U(s^N)}}$$

$$p(V) = \frac{\exp\left[-\beta\left(F(V) + PV\right)\right]}{Q_{NPT}}$$

$$Q_{NPT} = \beta P \int dV \exp\left[-\beta\left(F(V) + PV\right)\right]$$

$$\left\langle P \right\rangle = -\frac{\beta P}{Q(NPT)} \int dV \left(\frac{\partial F}{\partial V} \right)_{N,T} \exp\left[-\beta \left(F\left(V\right) + PV \right) \right]$$

$$\left\langle P \right\rangle = \frac{\beta P}{Q(NPT)} \int dV \, \frac{\exp\left[-\beta PV \right]}{\beta} \frac{\partial \exp\left[-\beta F\left(V\right) \right]}{\partial V}$$

Measured and Imposed Pressure

- Partial integration $\int_a^b f\, dg = [fg]_a^b - \int_a^b g\, df$

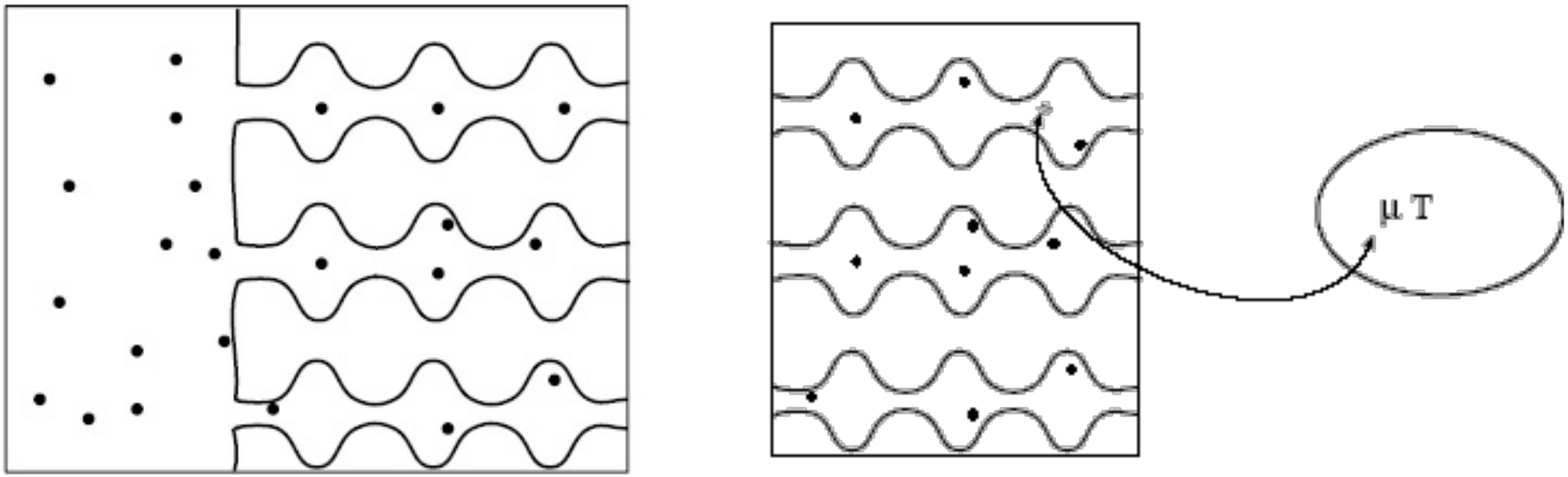
- For V=0 and V=∞ $\exp\left[-\beta\left(F\left(V\right)+PV\right)\right]=0$

- Therefore,

$$\langle P\rangle = \frac{\beta P}{Q(NPT)}\int dV\,\frac{\exp\left[-\beta PV\right]}{\beta}\frac{\partial \exp\left[-\beta F\left(V\right)\right]}{\partial V}$$

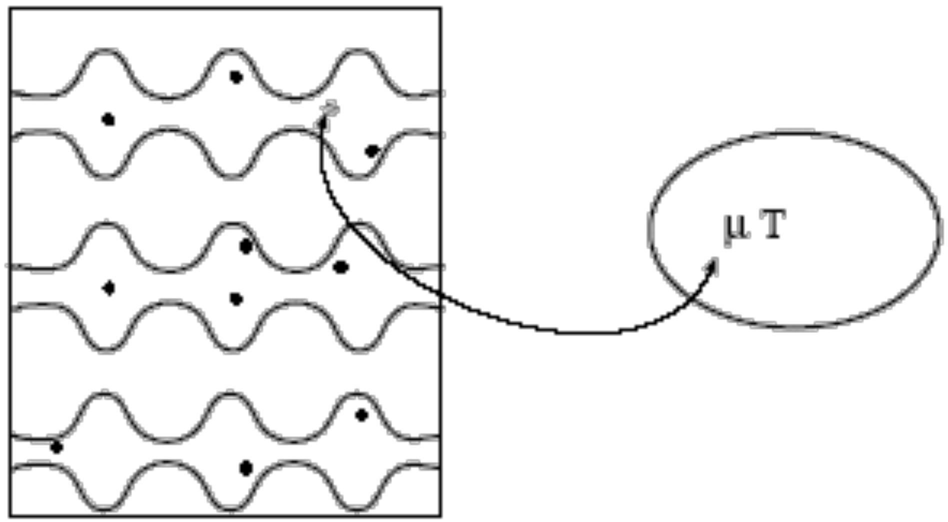
$$\langle P\rangle = \frac{\beta P}{Q(NPT)} = \int dVP\exp\left[-\beta\left(F\left(V\right)+PV\right)\right]=P$$

Grand-canonical ensemble



What are the equilibrium conditions?

Grand-canonical ensemble

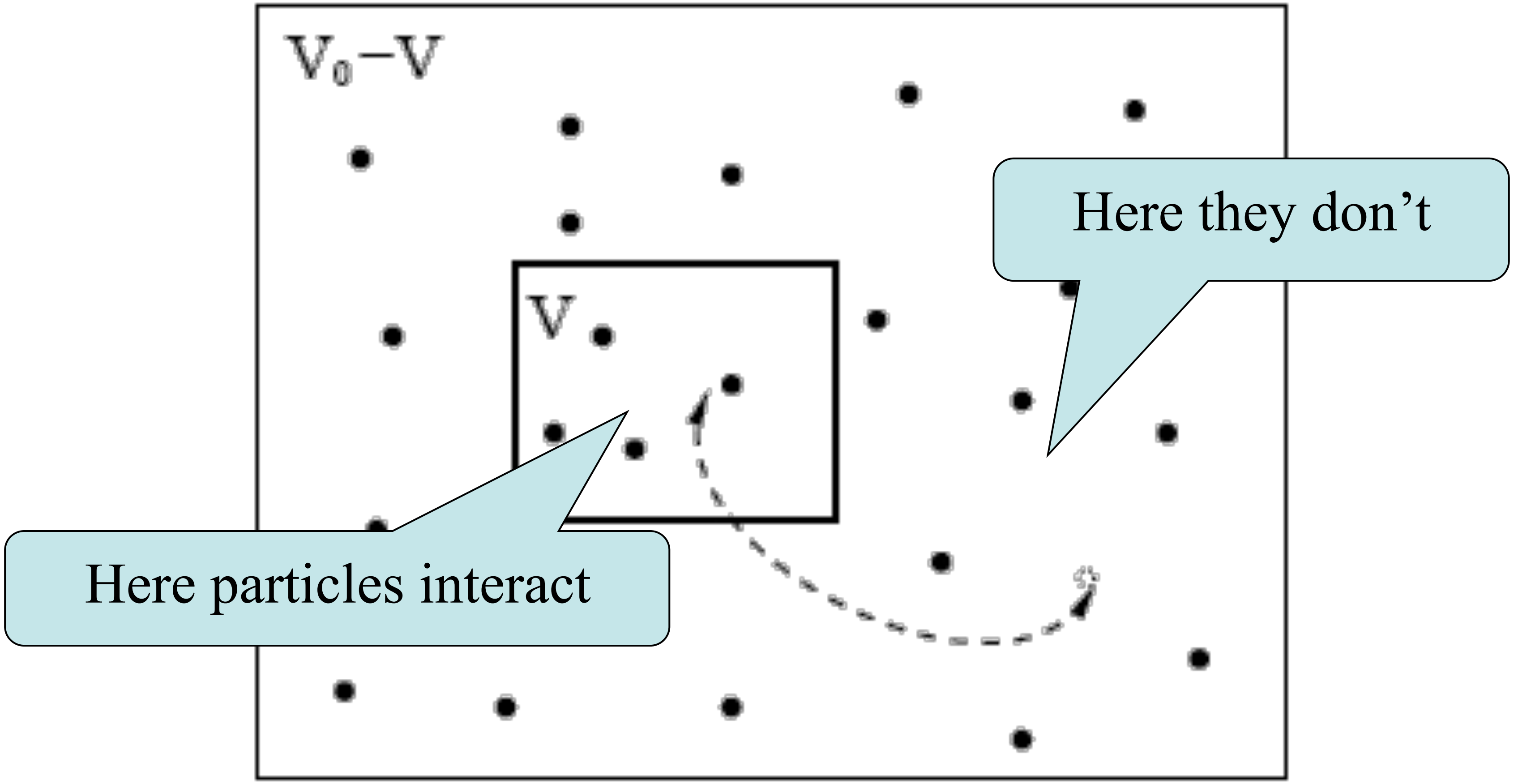


We impose:

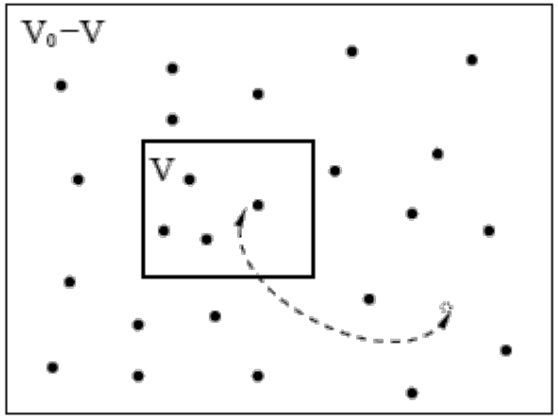
- Temperature (T)
- Chemical potential (μ)
- Volume (V)

- But **NOT** pressure

System in reservoir



What is the statistical thermodynamics of this ensemble?



$$Q_{NVT} = \frac{V^N}{\Lambda^{3N} N!} \int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

$$Q_{MV_0,NV,T} = \frac{\left(V_0 - V\right)^{M-N}}{\Lambda^{3(M-N)}\left(M-N\right)!} \int \mathrm{ds}^{M-V} \exp\left[-\beta U_0\left(\mathrm{s}^{M-N}; L\right)\right] \frac{V^N}{\Lambda^{3N} N!}$$

$$\times \int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

$$Q_{MV_0,NV,T} = \frac{\left(V_0 - V\right)^{M-N}}{\Lambda^{3(M-N)}\left(M-N\right)!}\frac{V^N}{\Lambda^{3N}N!}\int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N;L\right)\right]$$

To get the Partition Function of this system, we have to sum over all possible number of particles

$$Q_{MV_0,N,T} = \sum_{N=0}^{N=M}\frac{\left(V_0 - V\right)^{M-N}}{\Lambda^{3(M-N)}\left(M-N\right)!}\frac{V^N}{\Lambda^{3N}N!}\int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N;L\right)\right]$$

Now let us take the following limits:

$$\left.\begin{array}{l} M \to \infty \\ V_0 \to \infty \end{array}\right\} \rho = \frac{M}{V} \to \text{constant}$$

As the particles are an ideal gas in the big reservoir we have:

$$\mu = k_B T \ln\left(\Lambda^3 \rho\right)$$

$$Q_{\mu VT} = \sum_{N=0}^{N=\infty}\frac{\exp\left(\beta\mu N\right)V^N}{\Lambda^{3N}N!}\int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N;L\right)\right]$$

$$Q_{tot} = Q_R(M-N)Q_{sys}(N) = e^{-\beta F_R(M-N)}Q_{sys}(N)$$

Expand F_R

$$F_R(M-N) = F_R(M) - \left(\frac{\partial F_R}{\partial M}\right)N + \cdots$$

But: $\left(\frac{\partial F_R}{\partial M}\right) = \mu$ And hence:

$$Q_{tot} = Q_R(M-N)Q_{sys}(N) = e^{-\beta F_R(M)}e^{\beta\mu N}Q_{sys}(N)$$

Sum over all N:

$$Q_{\mu VT} = \sum_{N=0}^{N=\infty} \frac{\exp(\beta\mu N)V^N}{\Lambda^{3N}N!}\int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N;L\right)\right]$$

μVT Ensemble

Partition function:

$$Q_{\mu VT} = \sum_{N=0}^{N=\infty} \frac{\exp(\beta\mu N) V^N}{\Lambda^{3N} N!} \int \mathrm{ds}^N \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

Probability to find a particular configuration:

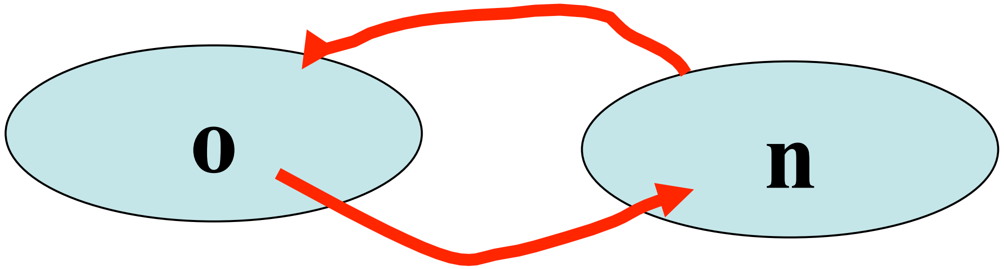
$$N_{\mu VT}\left(V, \mathbf{s}^N\right) \propto \frac{\exp(\beta\mu N) V^N}{\Lambda^{3N} N!} \exp\left[-\beta U\left(\mathrm{s}^N; L\right)\right]$$

Sample a particular configuration:

- Change of the number of particles
- Change of reduced coordinates

Acceptance rules ??

Detailed balance



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$$K(n \rightarrow o) = N(n) \times \alpha(n \rightarrow o) \times \text{acc}(n \rightarrow o)$$

$$\frac{\text{acc}(o \rightarrow n)}{\text{acc}(n \rightarrow o)} = \frac{N(n) \times \alpha(n \rightarrow o)}{N(o) \times \alpha(o \rightarrow n)} = \frac{N(n)}{N(o)}$$

μVT-ensemble

$$N_{\mu VT}\left(V,\mathbf{s}^{N}\right)\propto \frac{\exp\left(\beta\mu N\right)V^{N}}{\Lambda^{3N}N!}\exp\left[-\beta U\left(\mathrm{s}^{N};L\right)\right]$$

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)}=\frac{N(n)}{N(o)}$$

Suppose we change the position of a randomly selected particle

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)}=\frac{\frac{\exp\left(\beta\mu N\right)V^{N}}{\Lambda^{3N}N!}\exp\left[-\beta U\left(\mathrm{s}_{\mathrm{n}}^{\mathrm{N}};L\right)\right]}{\frac{\exp\left(\beta\mu N\right)V^{N}}{\Lambda^{3N}N!}\exp\left[-\beta U\left(\mathrm{s}_{\mathrm{o}}^{\mathrm{N}};L\right)\right]}$$

$$=\exp\left\{-\beta\left[U\left(n\right)-U\left(0\right)\right]\right\}$$

μVT-ensemble

$$N_{\mu VT}\left(V,\mathbf{s}^N\right)\propto \frac{\exp\left(\beta\mu N\right)V^N}{\Lambda^{3N}N!}\exp\left[-\beta U\left(\mathrm{s}^N;L\right)\right]$$

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)}=\frac{N(n)}{N(o)}$$

Suppose we change the ***number of particles*** of the system

$$\frac{\mathrm{acc}(o\rightarrow n)}{\mathrm{acc}(n\rightarrow o)}=\frac{\dfrac{\exp\left(\beta\mu\left(N+1\right)\right)V^{N+1}}{\Lambda^{3N+3}\left(N+1\right)!}\exp\left[-\beta U\left(\mathrm{s}^{N+1};L\right)\right]}{\dfrac{\exp\left(\beta\mu N\right)V^N}{\Lambda^{3N}N!}\exp\left[-\beta U\left(\mathrm{s}^{N};L\right)\right]}$$

$$=\frac{\exp\left(\beta\mu\right)V}{\Lambda^3\left(N+1\right)}\exp\left[-\beta\Delta U\right]$$

Algorithm 12 (Basic Grand-Canonical Ensemble Simulation)

```
 PROGRAM mc_gc                            basic μVT ensemble
                                          simulation
 do icycl=1,ncycl                         perform ncycl MC cycles
  ran=int(ranf()*(npav+nexc))+1
  if (ran.le.npart) then
    call mcmove                           displace a particle
  else
    call mcexc                            exchange a particle
  endif                                   with the reservoir
  if (mod(icycl,nsamp).eq.0)
+   call sample                           sample averages
 enddo
 end
```

Comments to this algorithm:

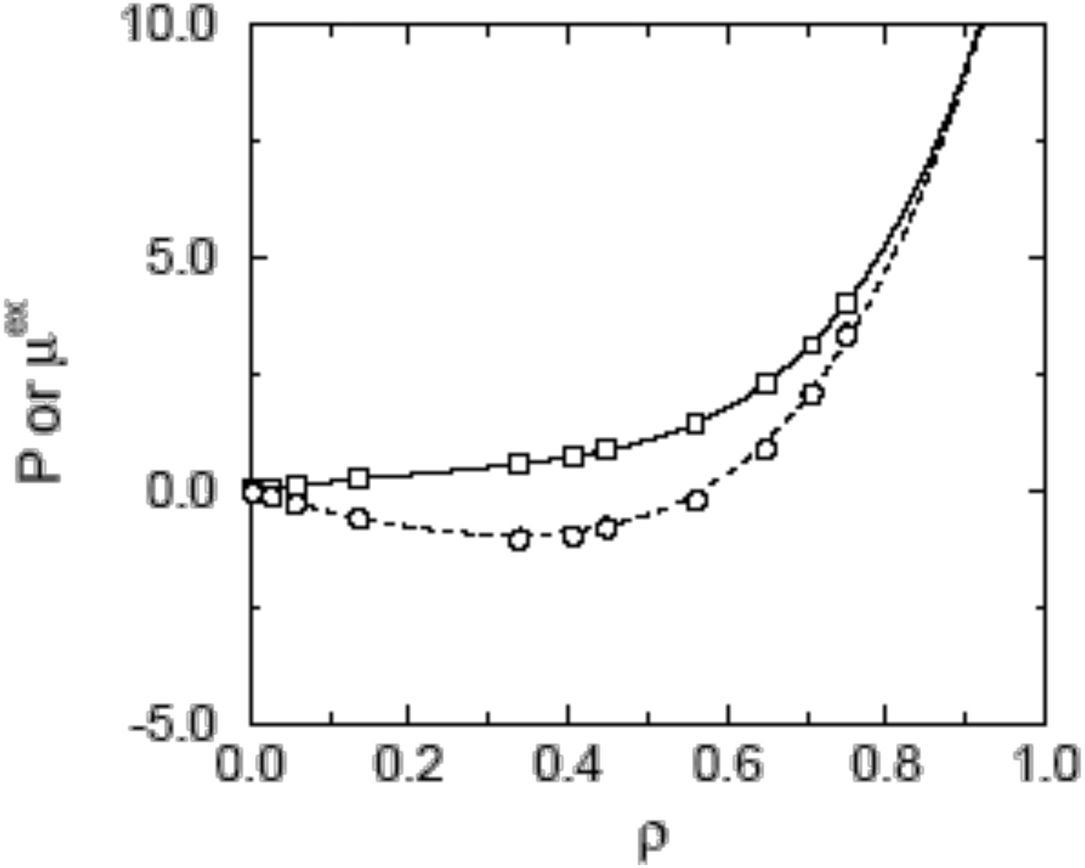
1. *This algorithm ensures that, after each MC step, detailed balance is obeyed. Per cycle we perform on average* `npav` *attempts*[6] *to displace particles and* `nexc` *attempts to exchange particles with the reservoir.*
2. *Subroutine* `mcmove` *attempts to displace a particle (Algorithm 2), subroutine* `mcexc` *attempts to exchange a particle with a reservoir (Algorithm 13), and subroutine* `sample` *samples quantities every* `nsamp` *cycle.*

Algorithm 13 (Attempt to Exchange a Particle with a Reservoir)

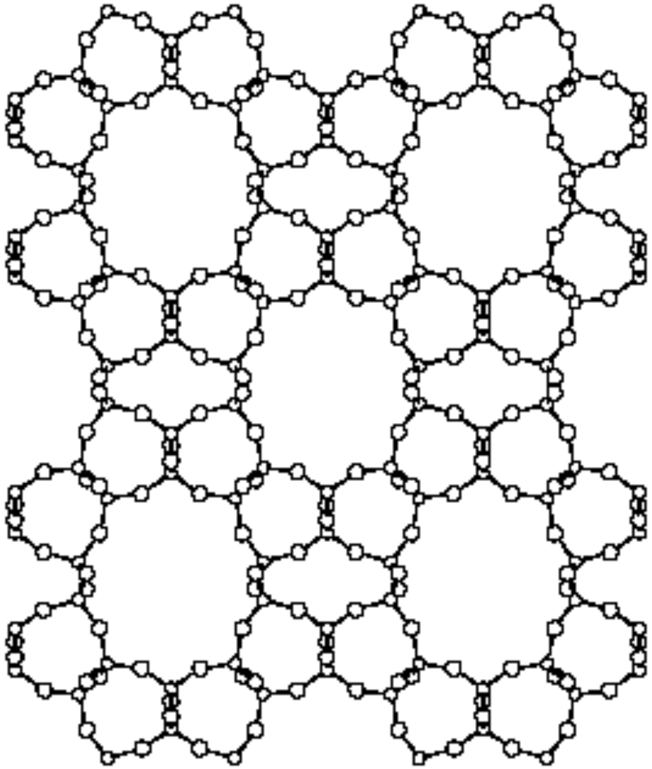
```
      SUBROUTINE mcexc                attempt to exchange a particle
                                      with a reservoir
      if (ranf().lt.0.5) then         decide to remove or add a particle
        if (npart.eq.0) return        test whether there is a particle
        o=int(npart*ranf())+1         select a particle to be removed
        call ener(x(o),eno)           energy particle o
        arg=npart*exp(beta*eno)       acceptance rule (5.6.9)
     +      /(zz*vol)
        if (ranf().lt.arg) then
          x(o)=x(npart)               accepted: remove particle o
          npart=npart-1
        endif
      else
        xn=ranf()*box                 new particle at a random position
        call ener(xn,enn)             energy new particle
        arg=zz*vol*exp(-beta*enn)     acceptance rule (5.6.8)
     +      /(npart+1)
        if (ranf().lt.arg) then
          x(npart+1)=xn               accepted: add new particle
          npart=npart+1
        endif
      endif
      return
      end
```

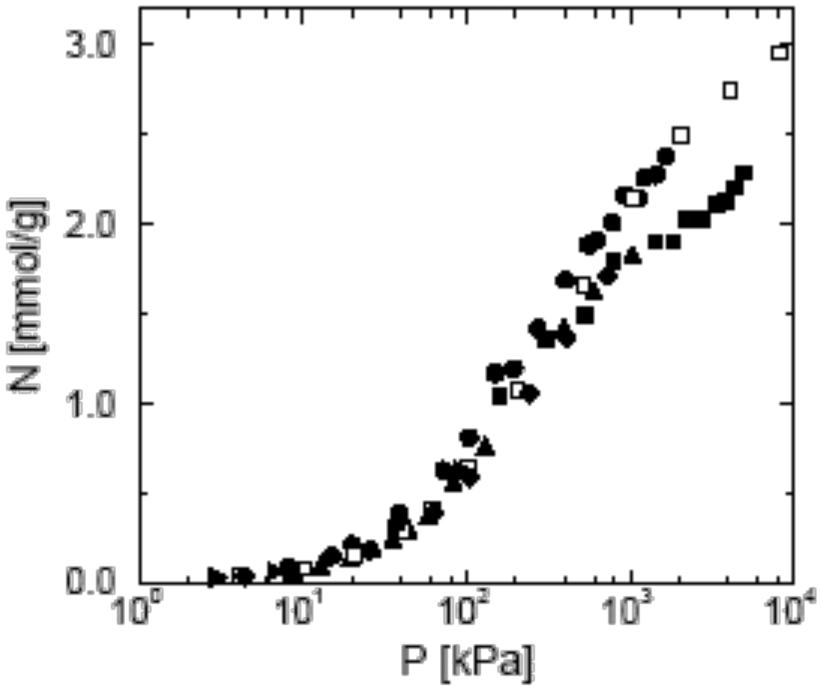
Comment to this algorithm:

Application: equation of state of Lennard-Jones



Application: adsorption in zeolites





Summary

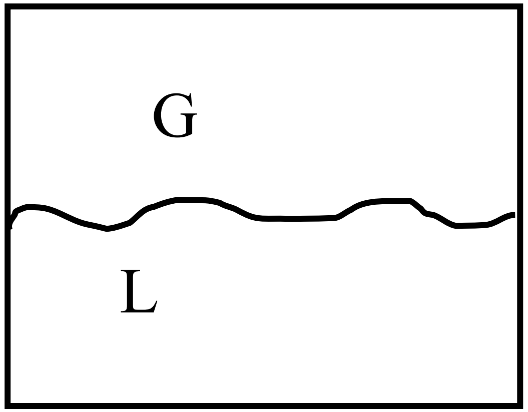
Ensemble	Constant (Imposed)	Fluctuating (Measured)	Function
NVT	N,V,T	P	$\beta F = -\ln Q(N,V,T)$
NPT	N,P,T	V	$\beta G = -\ln Q(N,P,T)$
μVT	μ,V,T	N	$\beta \Omega = -\ln Q(\mu,V,T) = -\beta PV$

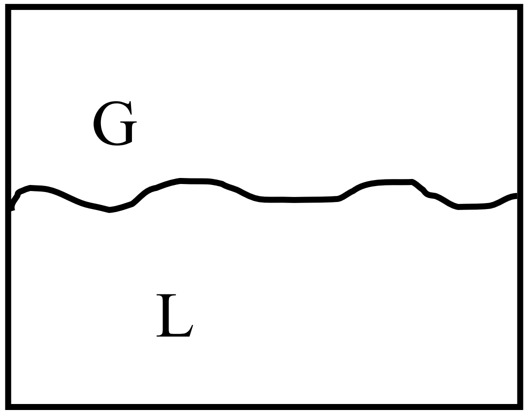
Studying phase coexistence:

The Gibbs “Ensemble”

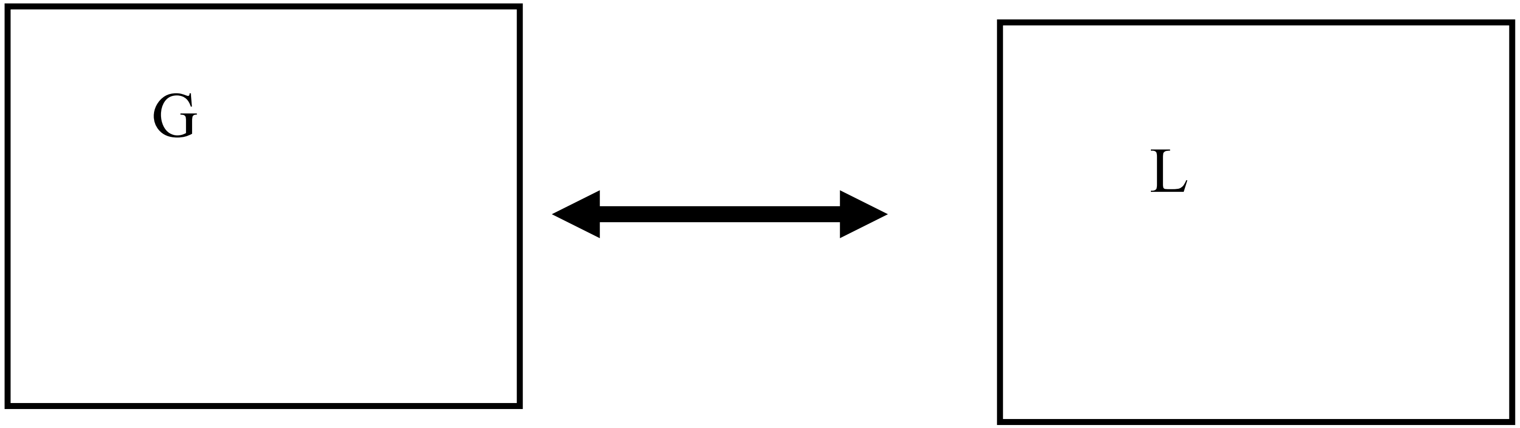
NVT Ensemble

NVT Ensemble

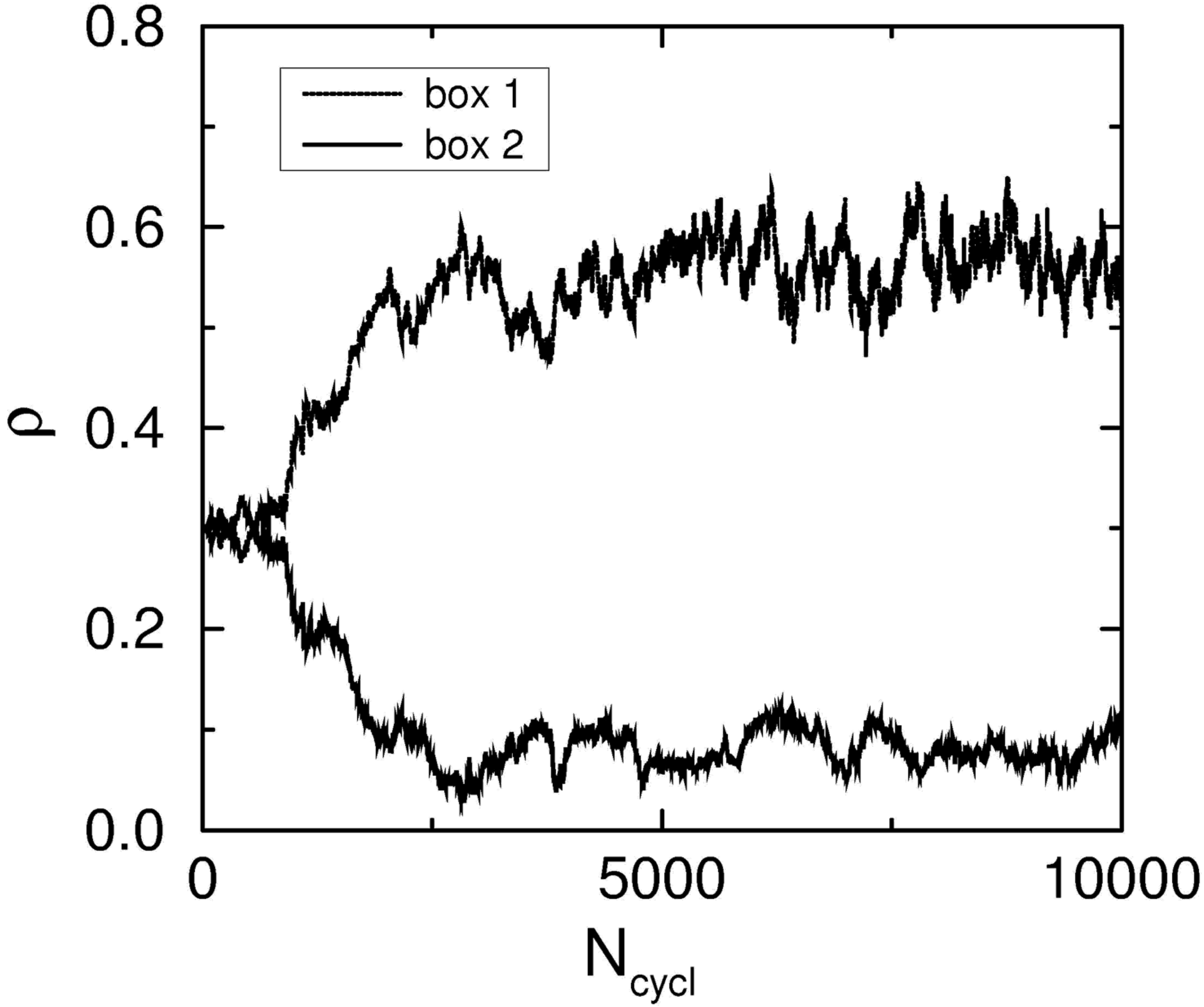




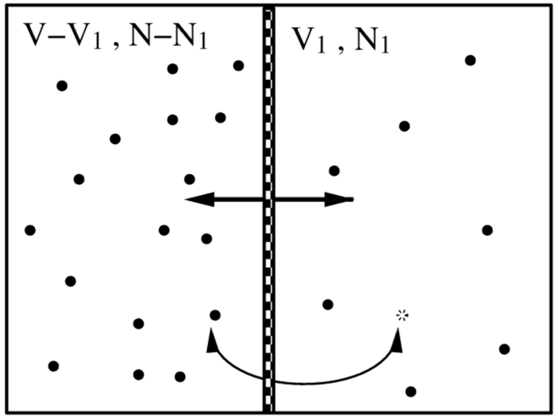
Gibbs Ensemble



Equilibrium!



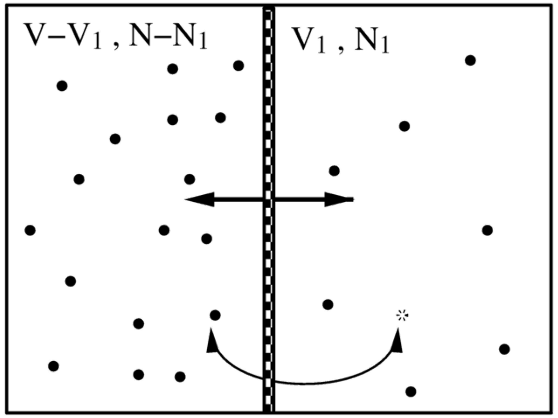
0.8
0.6
0.4
0.2
0.0
ρ
0
5000
10000
N_cycl
box 1
box 2



- Distribute n_1 particles over two volumes
- Change the volume V_1
- Displace the particles

$$Q_{\mathrm{G}}(N,V,T) \equiv \sum_{n_1=0}^{N} \frac{1}{V\Lambda^{3N} n_1!(N-n_1)!}\int_0^V dV_1\, V_1^{n_1}(V-V_1)^{N-n_1}$$

$$\int d\mathbf{s}_1^{n_1}\, \exp[-\beta U(\mathbf{s}_1^{n_1})]\int d\mathbf{s}_2^{N-n_1}\, \exp[-\beta U(\mathbf{s}_2^{N-n_1})]$$

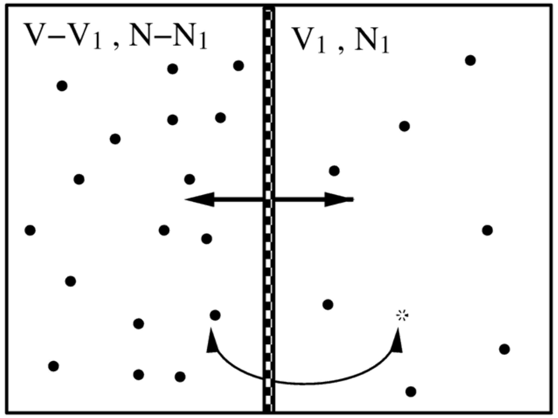


$$Q_G(N,V,T) \equiv \sum_{n_1=0}^{N} \frac{1}{V\Lambda^{3N} n_1!(N-n_1)!} \int_0^V dV_1\, V_1^{n_1} (V-V_1)^{N-n_1}$$

$$\int d\mathbf{s}_1^{n_1} \exp[-\beta U(\mathbf{s}_1^{n_1})] \int d\mathbf{s}_2^{N-n_1} \exp[-\beta U(\mathbf{s}_2^{N-n_1})]$$

Distribute n_1 particles over two volumes:

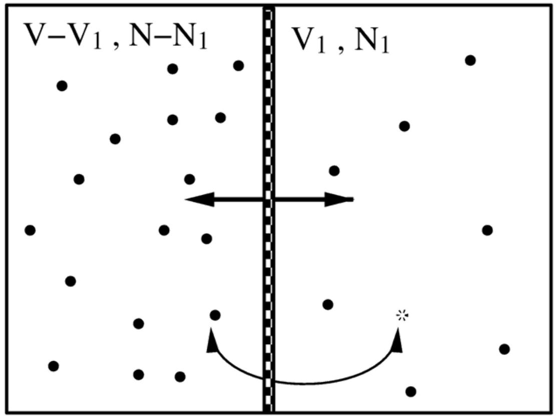
$$\binom{N}{n_1} = \frac{N!}{n_1!(N-n_1)!}$$



$$Q_G(N,V,T) \equiv \sum_{n_1=0}^{N} \frac{1}{V\Lambda^{3N} n_1!(N-n_1)!} \int_0^V dV_1\, V_1^{n_1} (V - V_1)^{N-n_1}$$

$$\int d\mathbf{s}_1^{n_1} \exp[-\beta U(\mathbf{s}_1^{n_1})] \int d\mathbf{s}_2^{N-n_1} \exp[-\beta U(\mathbf{s}_2^{N-n_1})]$$

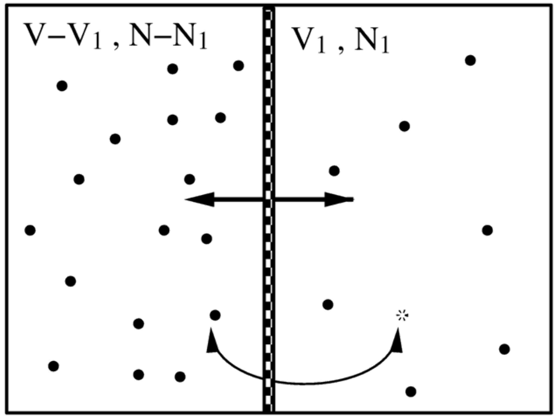
Integrate volume V_1



$$Q_G(N,V,T) \equiv \sum_{n_1=0}^{N} \frac{1}{V\Lambda^{3N} n_1!(N-n_1)!} \int_0^V dV_1 \, V_1^{n_1} (V - V_1)^{N-n_1}$$

$$\int d\mathbf{s}_1^{n_1} \exp[-\beta U(\mathbf{s}_1^{n_1})] \int d\mathbf{s}_2^{N-n_1} \exp[-\beta U(\mathbf{s}_2^{N-n_1})]$$

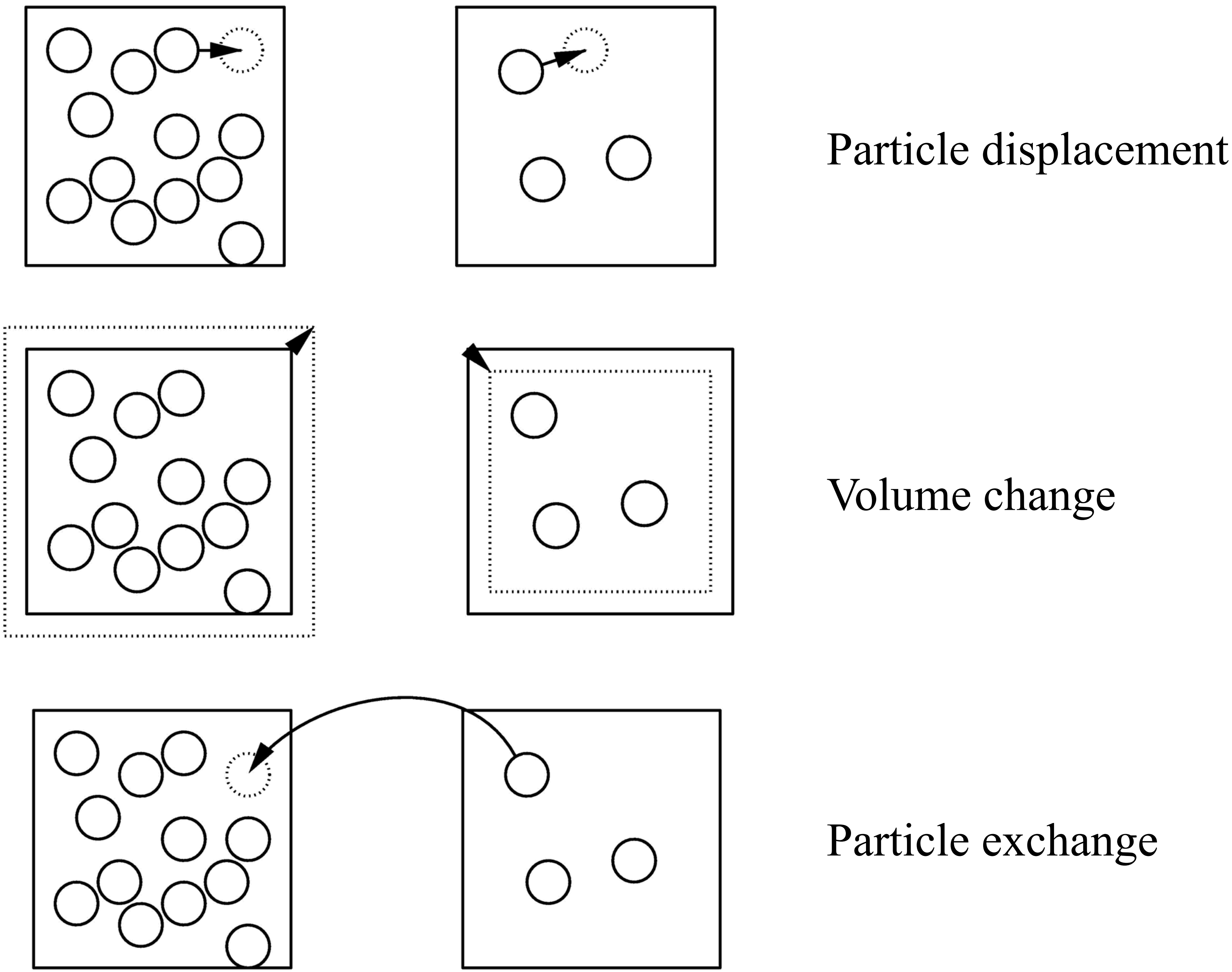
Displace the particles in box 1 and box2



$$Q_G(N,V,T) \equiv \sum_{n_1=0}^{N} \frac{1}{V\Lambda^{3N} n_1!(N-n_1)!} \int_0^V dV_1\, V_1^{n_1} (V - V_1)^{N-n_1}$$
$$\int d\mathbf{s}_1^{n_1} \exp[-\beta U(\mathbf{s}_1^{n_1})] \int d\mathbf{s}_2^{N-n_1} \exp[-\beta U(\mathbf{s}_2^{N-n_1})]$$

Probability distribution

$$N(n_1, V_1, \mathbf{s}_1^{n_1}, \mathbf{s}_2^{N-n_1}) \propto \frac{V_1^{n_1} (V - V_1)^{N-n_1}}{n_1!(N-n_1)!} \exp\left\{-\beta[U(\mathbf{s}_1^{n_1}) + U(\mathbf{s}_2^{N-n_1})]\right\}.$$


Particle displacement
Volume change
Particle exchange

Acceptance rules

$$N(n_1, V_1, \mathbf{s}_1^{n_1}, \mathbf{s}_2^{N-n_1}) \propto \frac{V_1^{n_1}(V - V_1)^{N-n_1}}{n_1!(N - n_1)!} \exp\left\{-\beta[U(\mathbf{s}_1^{n_1}) + U(\mathbf{s}_2^{N-n_1})]\right\}.$$

Detailed Balance:

$$K(o \to n) = K(n \to o)$$

$$N(o) \times \alpha(o \to n) \times \text{acc}(o \to n) = N(n) \times \alpha(n \to o) \times \text{acc}(n \to o)$$

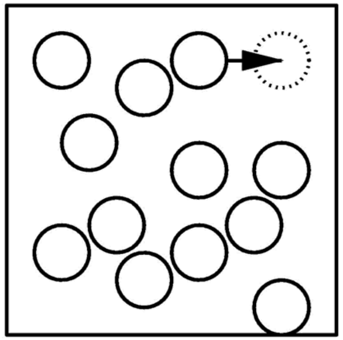
$$\frac{\text{acc}(o \to n)}{\text{acc}(n \to o)} = \frac{N(n) \times \alpha(n \to o)}{N(o) \times \alpha(o \to n)}$$

$$\frac{\text{acc}(o \to n)}{\text{acc}(n \to o)} = \frac{N(n)}{N(o)}$$

Displacement of a particle in box 1

$$N(n_1, V_1, \mathbf{s}_1^{n_1}, \mathbf{s}_2^{N-n_1}) \propto \frac{V_1^{n_1}(V - V_1)^{N-n_1}}{n_1!(N-n_1)!} \exp\left\{-\beta[U(\mathbf{s}_1^{n_1}) + U(\mathbf{s}_2^{N-n_1})]\right\}.$$

$$N(n) \propto \frac{V_1^{n_1}(V - V_1)^{N-n_1}}{n_1!(N-n_1)!} \exp\left\{-\beta[U_1(n) + U(\mathbf{s}_2^{N-n_1})]\right\}$$



$$N(o) \propto \frac{V_1^{n_1}(V - V_1)^{N-n_1}}{n_1!(N-n_1)!} \exp\left\{-\beta[U_1(o) + U(\mathbf{s}_2^{N-n_1})]\right\}$$

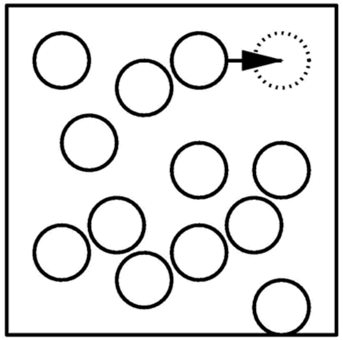
$$\frac{\mathrm{acc}(o \rightarrow n)}{\mathrm{acc}(n \rightarrow o)} = \frac{\frac{V_1^{n_1}(V - V_1)^{N-n_1}}{n_1!(N-n_1)!} \exp\left\{-\beta[U_1(n) + U(\mathbf{s}_2^{N-n_1})]\right\}}{\frac{V_1^{n_1}(V - V_1)^{N-n_1}}{n_1!(N-n_1)!} \exp\left\{-\beta[U_1(o) + U(\mathbf{s}_2^{N-n_1})]\right\}}$$

Displacement of a particle in box 1

$$N(n_1, V_1, \mathbf{s}_1^{n_1}, \mathbf{s}_2^{N-n_1}) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!} \exp\left\{-\beta\left[U(\mathbf{s}_1^{n_1}) + U(\mathbf{s}_2^{N-n_1})\right]\right\}.$$

$$N(n) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!} \exp\left\{-\beta\left[U_1(n) + U(\mathbf{s}_2^{N-n_1})\right]\right\}$$

$$N(o) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!} \exp\left\{-\beta\left[U_1(o) + U(\mathbf{s}_2^{N-n_1})\right]\right\}$$



$$\frac{\mathrm{acc}(o \rightarrow n)}{\mathrm{acc}(n \rightarrow o)} = \frac{\exp\left\{-\beta\left[U_1(n)\right]\right\}}{\exp\left\{-\beta\left[U_1(o)\right]\right\}}$$

Acceptance rules

$$N(n_1, V_1, \mathbf{s}_1^{n_1}, \mathbf{s}_2^{N-n_1}) \propto \frac{V_1^{n_1}(V - V_1)^{N-n_1}}{n_1!(N-n_1)!} \exp\left\{-\beta[U(\mathbf{s}_1^{n_1}) + U(\mathbf{s}_2^{N-n_1})]\right\}.$$

Adding a particle to box 2

$$N(n) \propto \frac{V_1^{n_1-1}(V - V_1)^{N-(n_1-1)}}{(n_1-1)!\left(N-(n_1-1)\right)!} \exp\left\{-\beta[U_1(n) + U_2(n)]\right\}$$

$$N(o) \propto \frac{V_1^{n_1}(V - V_1)^{N-n_1}}{n_1!(N-n_1)!} \exp\left\{-\beta[U_1(o) + U_2(o)]\right\}$$

$$\frac{\text{acc}(o \rightarrow n)}{\text{acc}(n \rightarrow o)} = \frac{N(n)}{N(o)}$$

Moving a particle from box 1 to box 2

$$N(n) \propto \frac{V_1^{n_1-1}(V-V_1)^{N-(n_1-1)}}{(n_1-1)!\left(N-(n_1-1)\right)!}\exp\left\{-\beta[U_1(n)+U_2(n)]\right\}$$

$$N(o) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}\exp\left\{-\beta[U_1(o)+U_2(o)]\right\}$$

$$\frac{\mathrm{acc}(o \rightarrow n)}{\mathrm{acc}(n \rightarrow o)} = \frac{\dfrac{V_1^{n_1-1}(V-V_1)^{N-(n_1-1)}}{(n_1-1)!\left(N-(n_1-1)\right)!}\exp\left\{-\beta[U_1(n)+U_2(n)]\right\}}{\dfrac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}\exp\left\{-\beta[U_1(o)+U_2(o)]\right\}}$$

Moving a particle from box 1 to box 2

$$N(n) \propto \frac{V_1^{n_1-1}(V-V_1)^{N-(n_1-1)}}{(n_1-1)!\left(N-(n_1-1)\right)!}\exp\left\{-\beta[U_1(n)+U_2(n)]\right\}$$

$$N(o) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}\exp\left\{-\beta[U_1(o)+U_2(o)]\right\}$$

$$\frac{\mathrm{acc}(o\to n)}{\mathrm{acc}(n\to o)} = \frac{\dfrac{V_1^{n_1-1}(V-V_1)^{N-(n_1-1)}}{(n_1-1)!\left(N-(n_1-1)\right)!}\exp\left\{-\beta[U_1(n)+U_2(n)]\right\}}{\dfrac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}\exp\left\{-\beta[U_1(o)+U_2(o)]\right\}}$$

Moving a particle from box 1 to box 2

$$N(n) \propto \frac{V_1^{n_1-1}(V-V_1)^{N-(n_1-1)}}{(n_1-1)!\left(N-(n_1-1)\right)!}\exp\left\{-\beta[U_1(n)+U_2(n)]\right\}$$

$$N(o) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}\exp\left\{-\beta[U_1(o)+U_2(o)]\right\}$$

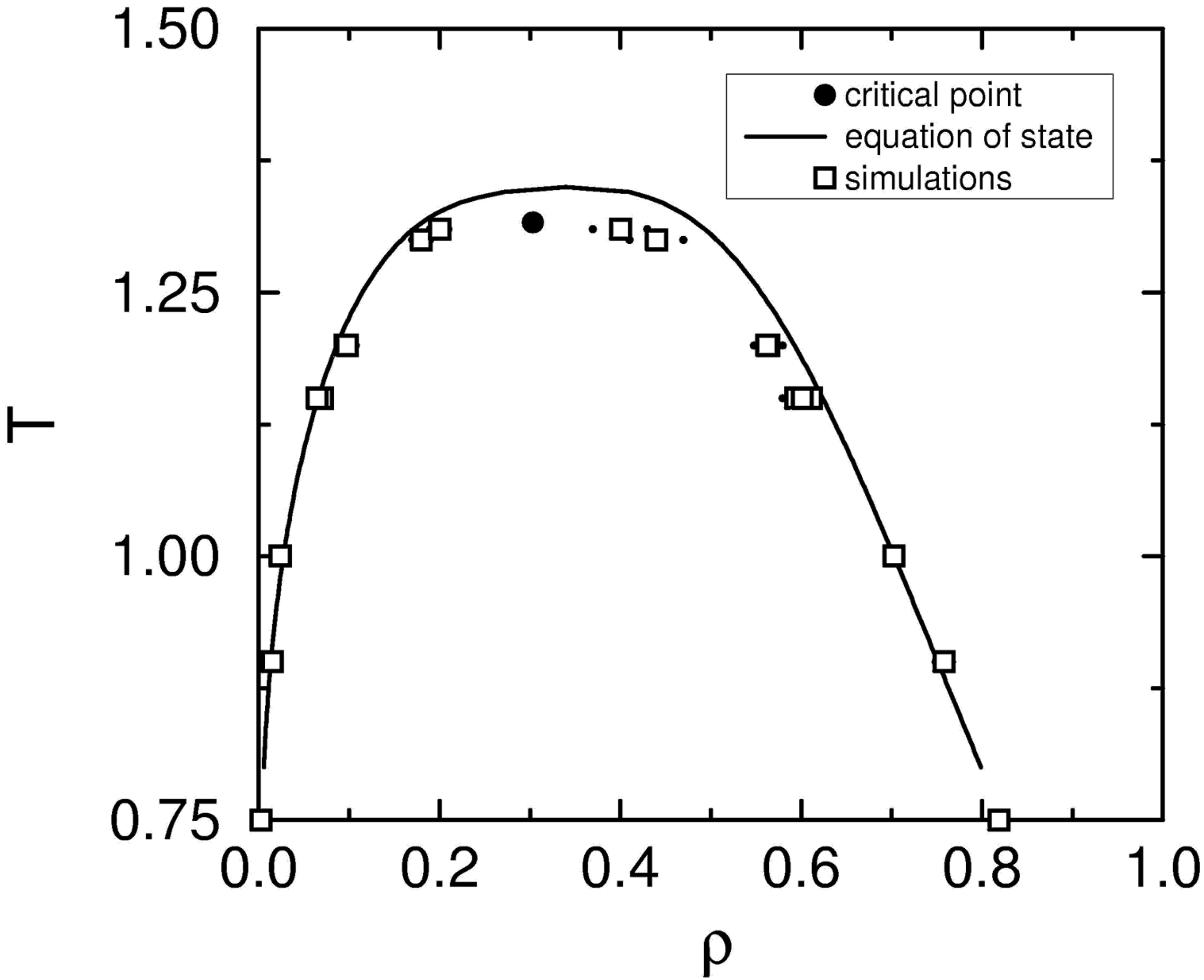
$$\frac{\mathrm{acc}(o\to n)}{\mathrm{acc}(n\to o)} = \frac{\dfrac{V_1^{n_1-1}(V-V_1)^{N-(n_1-1)}}{(n_1-1)!\left(N-(n_1-1)\right)!}\exp\left\{-\beta[U_1(n)+U_2(n)]\right\}}{\dfrac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}\exp\left\{-\beta[U_1(o)+U_2(o)]\right\}}$$

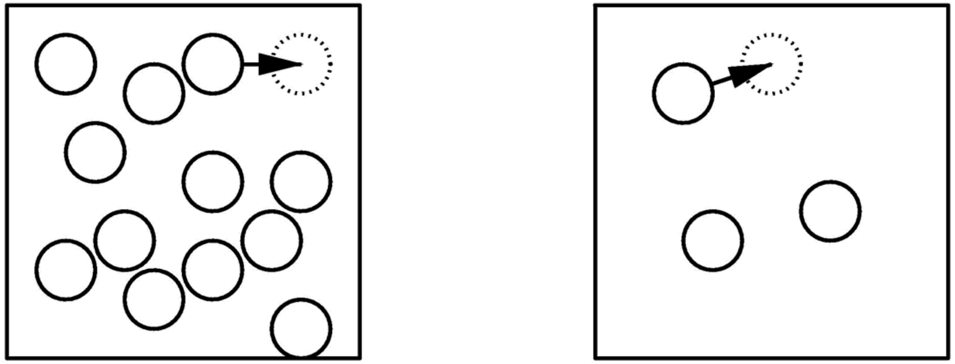
Moving a particle from box 1 to box 2

$$N(n) \propto \frac{V_1^{n_1-1}(V-V_1)^{N-(n_1-1)}}{(n_1-1)!\left(N-(n_1-1)\right)!}\exp\left\{-\beta[U_1(n)+U_2(n)]\right\}$$

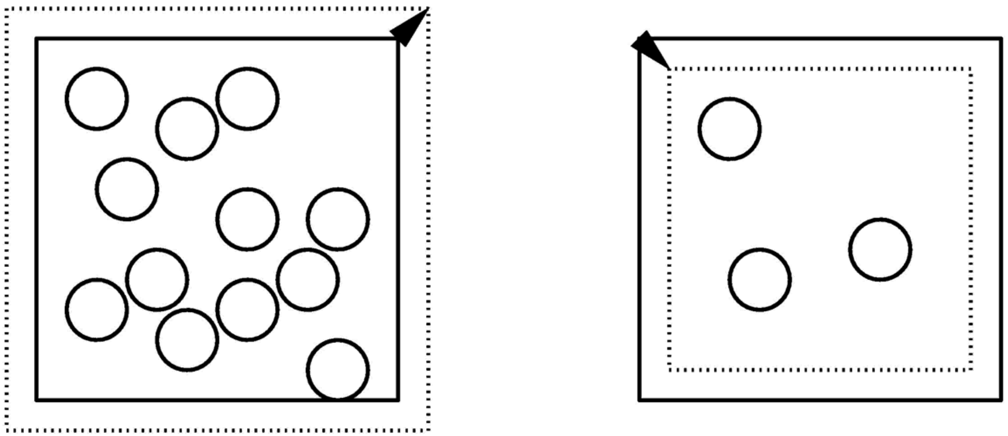
$$N(o) \propto \frac{V_1^{n_1}(V-V_1)^{N-n_1}}{n_1!(N-n_1)!}\exp\left\{-\beta[U_1(o)+U_2(o)]\right\}$$

$$\frac{\text{acc}(o \rightarrow n)}{\text{acc}(n \rightarrow o)} = \frac{\frac{V_2}{n_2+1}}{\frac{V_1}{n_1}}\exp\left\{-\beta[\Delta U_1 + \Delta U_2]\right\}$$

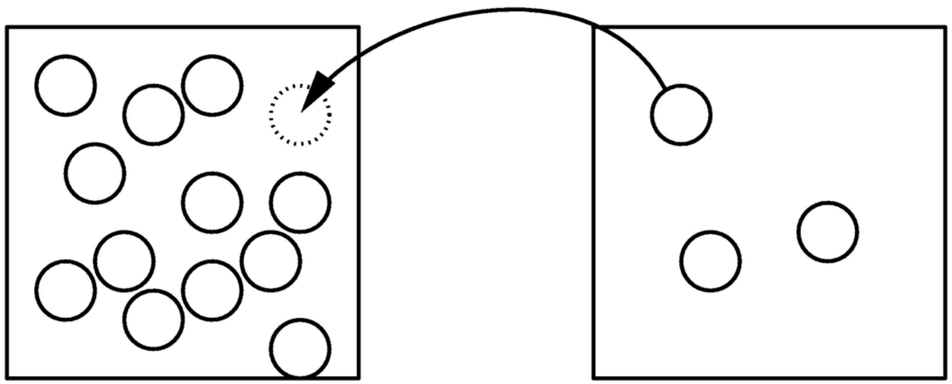

1.50
1.25
1.00
0.75
T
0.0
0.2
0.4
0.6
0.8
1.0
ρ
critical point
equation of state
simulations



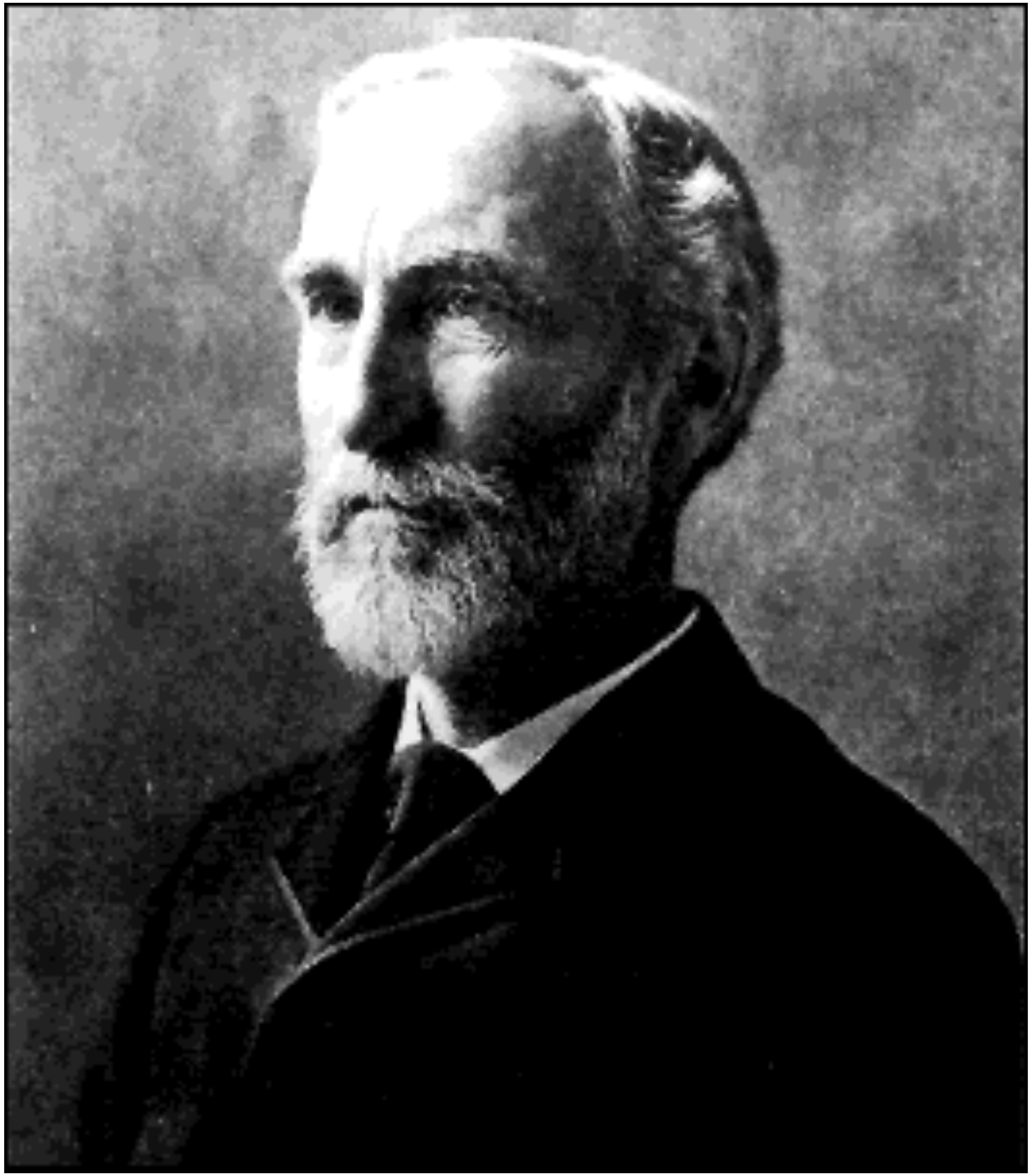
Particle displacements
(to sample
configuration space)



Volume exchanges
(to impose equality
of pressures)



Particle exchanges
(to impose equality
of chemical potetials)



N! and the Gibbs Paradox

$$Q_{NVT} = \frac{1}{\Lambda^{3N} N!} \int \mathrm{d}\mathrm{r}^N \exp\left[-\beta U\left(\mathrm{r}^N\right)\right].$$

QUESTION:

Can we use this expression for systems of distinguishable particles – e.g. colloidal suspensions?

What do the textbooks say?

Thus, it seems that the $1/N!$ term is absolutely necessary to resolve the paradox. This means that only a correct quantum mechanical treatment of the ideal gas gives rise to a consistent entropy.

could only later be identified with Planck's constant h. The indistinguishability of particles of the same kind, which had to be introduced in order to avoid the *Gibbs' paradox*,[1] got a firm logical basis only after the invention of quantum theory. The observed distribution of black-body radiation could

least one nucleon mass). Hence the distinction between identical and non-identical molecules is completely unambiguous in a quantum-mechanical description. The Gibbs paradox thus foreshadowed already in the last century conceptual difficulties that were resolved satisfactorily only by the advent of quantum mechanics.

It is not possible to understand classically why we must divide $\Sigma(E)$ by N! to obtain the correct counting of states. The reason is inherently quantum mechanical. Quantum mechanically, atoms are inherently indistinguishable in the following sense: A state of the gas is described by an N-particle wave function, which is either symmetric or antisymmetric with respect to the interchange of any

LANDAU & LIFSHITZ
footnote

† This becomes particularly evident if we consider the classical partition function (integral over states) as the limit of the quantum partition function. In the latter the summation is over all the different quantum states, and there is no problem (remembering that, because of the principle of symmetry of wave functions in quantum mechanics, the quantum state is unaffected by interchanges of identical particles).

From the purely classical viewpoint the need for this interpretation of the statistical integration arises because otherwise the statistical weight would no longer be multiplicative, and so the entropy and the other thermodynamic quantities would no longer be additive.

Van Kampen

In *statistical mechanics* this dependence is obtained by inserting a factor $1/N!$ in the partition function. Quantum mechanically this factor enters automatically and in many textbooks that is the way in which it is justified. My point is that this is irrelevant: *even in classical statistical mechanics it can be derived by logic* — rather than by the somewhat mystical arguments of Gibbs [2] and Planck.[3,4] Specifically I take exception to such statements as: "It is not possible to understand classically why we must divide by $N!$ to obtain the correct counting of states",[5] and: "Classical statistics thus leads to a contradiction with experience even in the range in which quantum effects in the proper sense can be completely neglected".[6]

ENTER JAYNES:

“Usually, Gibbs’ prose style conveys his meaning in a sufficiently clear way…”

“… using no more than twice as many words as Poincaré or Einstein would have used to say the same thing”

“But occasionally he delivers a sentence with a ponderous unintelligibility that seems to challenge us to make sense out of it…”

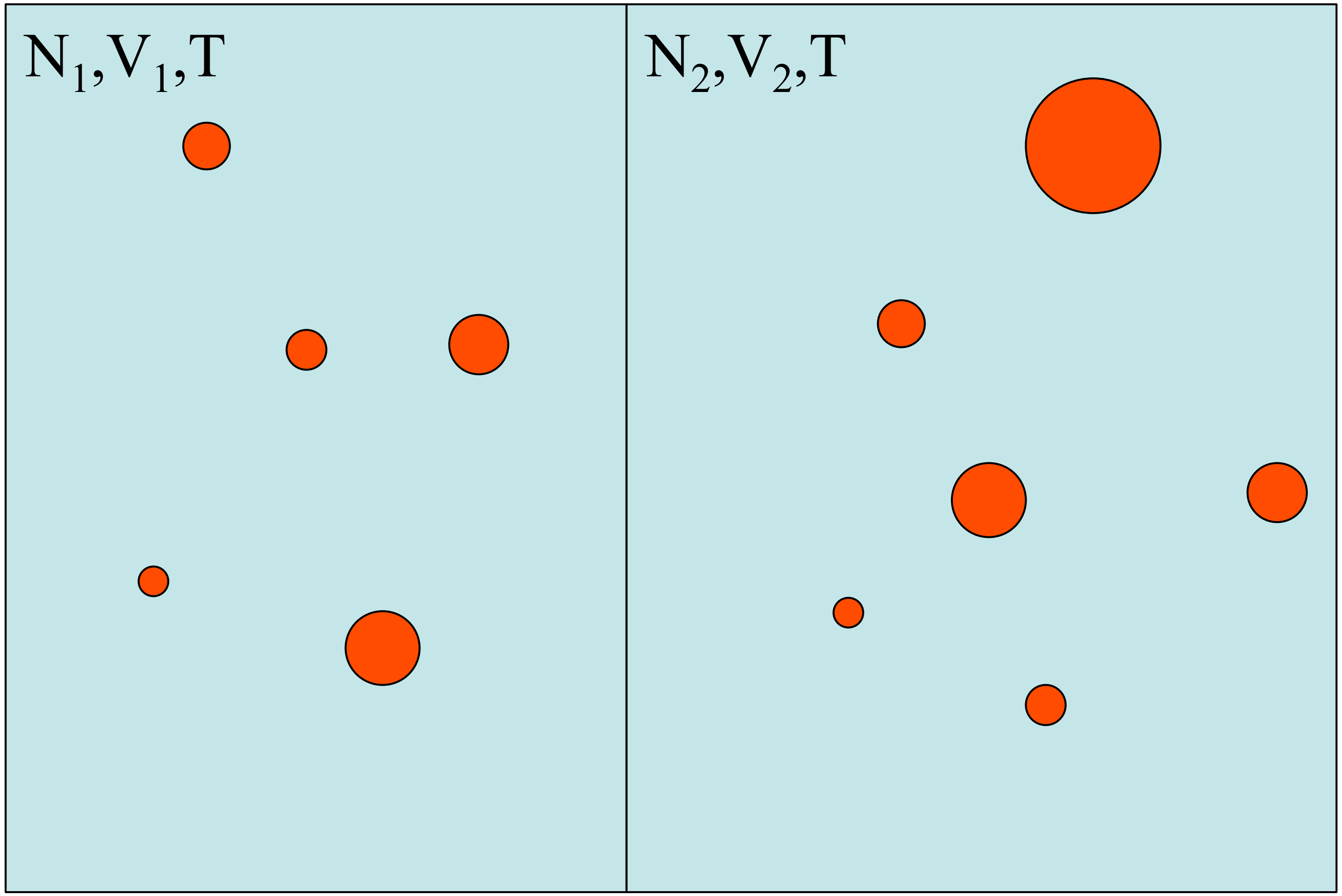
GIBBS's SENTENCE:

“Again, when such gases have been mixed, there is no more impossibility of the separation of the two kinds of molecules in virtue of their ordinary motion in the gaseous mass without any especial external influence, than there is of the separation of a homogeneous gas into the same two parts into which it has once been divided, after these have these have once been mixed”

Elsewhere, Gibbs says:

As long as the **number of particles** is kept **fixed**, inclusion of the factor N! is **optional**.

However, when comparing systems with **different number of particles, you MUST include N!** to obtain an extensive entropy.



Two systems of `identical' dilute colloidal solutions in equilibrium (low-fat milk).

ln Z **is not extensive**

Treat as gas of N labeled *but otherwise ident*

$$Z_{dist}(N) = V^N$$

Now: two such systems with N_1 and N_2 particles. In equilibrium, we can distribute the particles over the two systems in any way we choose (with fixed N_1 and N_2).

$$Z_{combined}(N_1, V_1, N_2, V_2) = V_1^{N_1} V_2^{N_2} \times \frac{(N_1 + N_2)!}{N_1! N_2!}$$

NOTE:

1. all particles are different (they just have identical properties – e.g. monodisperse colloidal spheres)
2. $Z_{combined}$ is **not** extensive. Not even in quantum mechanics.

When the two systems are in equilibrium, the partition function is maximal with respect to variations in N_1 ($dN_1=-dN_2$).

$$\left(\frac{\partial \ln Z_c}{\partial N_1}\right)_N = \frac{\partial \ln Z_1/N_1!}{\partial N_1} - \frac{\partial \ln Z_2/N_2!}{\partial N_2} = 0$$

Therefore, as soon as we are computing the **chemical potential**, we MUST include the factor N!, also for labeled particles.

Conveniently, the partition function of the combined system then factorizes

$$\frac{Z_c(N_1, V_1, N_2, V_2)}{(N_1 + N_2)!} = \frac{Z_1}{N_1!} \frac{Z_2}{N_2!}$$

and hence the free energy is extensive.

$$\ln\left(\frac{Z_c(N_1, V_1, N_2, V_2)}{(N_1 + N_2)!}\right) = \ln\left(\frac{Z_1}{N_1!}\right) + \ln\left(\frac{Z_2}{N_2!}\right)$$

“Quantum” indistinguishability of identical particles is true, but usually irrelevant (as any colloid scientist knows).

Reference:

Why colloidal systems can be described by statistical mechanics: some not very original comments on the Gibbs paradox

D. Frenkel, Mol. Phys. **112**, 2325–2329 (2014)